

1 ALD DEPOSITION OF RUTHENIUM

2
3 FIELD OF THE INVENTION

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5 This invention relates to electrical interconnection
6 structures. More particularly, it relates to "back end
7 of the line" (BEOL) interconnections in high
8 performance integrated circuits, and to advanced CMOS
9 device fabrication.

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11 BACKGROUND OF THE INVENTION

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13 Electrodeposition of copper is a standard
14 deposition technique used for copper interconnect
15 applications. However, copper cannot be electroplated
16 directly onto diffusion barrier materials without a
17 thin copper seed layer. In current processes, the
18 copper seed layers are deposited by Physical Vapor
19 Deposition (PVD) for this purpose, often by derivative
20 techniques of ionized PVD (I-PVD). However, in future
21 semiconductor generations, a very conformal film
22 deposition in nanoscale, high aspect ratio structures
23 will be required. This may only be achievable only by
24 Atomic Layer Deposition (ALD) techniques. As an
25 alternative, copper electrodeposition can be also done
26 on other low-resistance metal surfaces. The required
27 material properties for this purpose include nobility,
28 formation of soluble or conducting oxides, and
29 insolubility in the copper bath. Preferably, direct
30 plating materials have good diffusion barrier
31 properties as well as good adhesion to dielectrics. A
32 few metal layers have been identified as candidates,

1 which are generally refractory metals such as Ru, Rh,
2 Co, Mo, Cr, and W.

3
4 Recently, ruthenium is receiving attention as a
5 directly plateable material due to its good properties
6 as an electrode in DRAM applications, as a metal gate
7 for CMOS applications, and its application as a seed
8 layer for direct plating of copper using an
9 electroplating process.

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11 Ruthenocene (or ruthenium cyclopentadienyl, $\text{Ru}(\text{C}_5\text{H}_5)_2$),
12 otherwise known as $\text{Ru}(\text{Cp})_2$, has been used as a metal
13 precursor which is reacted with molecular oxygen to
14 produce ruthenium thin films by ALD. Polycrystalline
15 ruthenium films with quite low resistivity (12-13
16 $\mu\Omega\text{cm}$) were obtained with low impurity levels. However,
17 due to a nucleation problem associated with the metal
18 organic ruthenium precursor, only a very limited,
19 non-uniform deposition occurs on some dielectric
20 surfaces, including silicon dioxide (SiO_2). To overcome
21 this problem, the prior art used an *in situ* grown
22 aluminum oxide (Al_2O_3) layer before ALD of ruthenium.
23 There has been no know solution for direct deposition
24 of ruthenium by ALD on SiO_2 and other dielectric
25 surfaces. Even for CVD of ruthenium on oxides, it is a
26 common practice to first deposit a ruthenium seed layer
27 by PVD. For the implementation of ruthenium by ALD to
28 device processing, especially for direct plating and
29 metal gate purpose, some way of depositing metallic

1 ruthenium films directly on to dielectrics is
2 essential.

3

4 Due to the RC delay in nanoscale integrated circuits,
5 novel low dielectric constant (low k) materials are
6 being introduced. It has been widely known that vapor
7 phase deposition including chemical vapor deposition
8 (CVD) and ALD generally have nucleation problems on
9 these low k dielectrics. However, as the required film
10 thickness of liner materials, including direct plating
11 liners, is getting thinner as the device scaling
12 entering sub-100 nanometer technological node size, a
13 nucleation problem could be a potentially serious
14 matter. Thus, various surface treatment technique to
15 deposit metal thin films on dielectrics without
16 nucleation during the ALD of ruthenium is essential for
17 implementing ALD of metals as direct plating
18 applications, as well as liner applications, in the
19 BEOL area.

20

21 In another application of ruthenium ALD, the metal gate
22 process require direct deposition of ruthenium on thin
23 SiO₂ or high k materials. Ruthenium has been
24 considered one of candidates for the metal gate of dual
25 gate CMOS devices due to its work function having the
26 proper value.

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1 SUMMARY OF THE INVENTION

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3 It is therefore an aspect of the present invention to
4 provide a method for forming a layer of ruthenium on a
5 substrate which is free of nucleation problems.

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7 It is another object of the present invention to form a
8 layer of ruthenium on a substrate which has a low
9 concentration of impurities such as oxygen and carbon.

10 A feature of the invention is the elimination of
11 nucleation issue during ruthenium film ALD on
12 dielectric surfaces, such as SiO_2 . The invention
13 relates to the use of a nucleation aiding layer
14 deposited by plasma-enhanced ALD by using a ruthenium
15 metal organic precursor and atomic hydrogen. Once the
16 underlayer of ruthenium film is formed, thermal
17 ruthenium ALD using molecular oxygen instead of
18 hydrogen plasma is employed to deposit ruthenium with
19 very low impurity levels of carbon or oxygen.

20

21 After proper plasma treatment, the ruthenium metal
22 films are deposited on SiO_2 without nucleation
23 problems. The various surface treatment techniques,
24 generally using plasma treatment prior to the atomic
25 layer deposition of ruthenium metal on dielectrics,
26 results in ruthenium deposition by ALD which is free of
27 nucleation problems.

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29 Thus, the invention is directed to a method for
30 depositing ruthenium on a substrate, comprising

1 exposing the substrate to a plasma which causes a high
2 concentration of nucleation sites to be formed on the
3 substrate, thus forming an exposed substrate; and
4 depositing ruthenium on the exposed substrate by atomic
5 layer deposition. The substrate is selected may be
6 selected from the group consisting of silicon dioxide,
7 methyl silsesquioxane, hydrogen silsesquioxane, low
8 dielectric constant materials, and high dielectric
9 constant oxide substrates.

10
11 The plasma is may be an oxygen plasma, and may be
12 generated by passing molecular oxygen through a plasma
13 generation source to produce activated radicals to
14 thereby generate a large number of nucleation sites on
15 the substrate. The plasma may also be a nitrogen and
16 may be generated by passing molecular nitrogen through
17 a plasma generation source to produce activated
18 radicals to thereby generate a large number of
19 nucleation sites on the substrate.

20
21 The atomic layer deposition may be performed by
22 alternating steps of exposing the substrate to a
23 ruthenium precursor for a first predetermined period of
24 time; and exposing the substrate to a plasma for a
25 second predetermined time. The method further
26 comprising evacuating the ruthenium precursor and the
27 plasma between successive steps.

28
29 The ruthenium precursor is selected may be selected
30 from the group consisting of:

1 ruthenium cyclopentadienyl,
2 bis (ethylcyclopentadienyl) ruthenium); and
3 ((2,4-dimethylpentadienyl)ethylcyclopentadienyl) ruth-
4 enium). The ruthenium precursor is carried in a
5 carrier gas, preferably inert, such as argon.
6

7 The substrate may be heated to a temperature of between
8 200 and 400 °C, and preferably, 350 °C.
9

10 Using this method the ruthenium is deposited directly
11 on the substrate without use of a seed layer.
12

13 In accordance with another aspect of the invention, a
14 method for depositing ruthenium on a substrate,
15 comprises performing plasma enhanced atomic layer
16 deposition of ruthenium on the substrate using a
17 ruthenium precursor and a plasma to form a thin film of
18 ruthenium; and depositing ruthenium on the thin film by
19 thermal atomic layer deposition. The plasma is
20 preferably a hydrogen plasma. As set forth above, the
21 atomic layer deposition is performed by alternating
22 steps of exposing the substrate to a ruthenium
23 precursor for a first predetermined period of time; and
24 exposing the substrate to a plasma for a second
25 predetermined time. The process may employ the
26 parameters and conditions set forth in detail above.
27

28 In accordance with yet another aspect of the invention,
29 a ruthenium film formed by atomic layer deposition
30 comprises less than three percent oxygen and less than

1 2 % carbon. The film may be configured as a gate of a
2 CMOS device. The film may be deposited on a silicon
3 dioxide substrate. The ruthenium film may be deposited
4 directly on a substrate without use of a seed layer.
5 The film may serve as a plating layer for a copper
6 interconnect.

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9 BRIEF DESCRIPTION OF THE DRAWINGS

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11 These and other aspects, features, and advantages of
12 the present invention will become apparent upon further
13 consideration of the following detailed description of
14 the invention when read in conjunction with the drawing
15 figures, in which:

16
17 Fig. 1A illustrates deposited ruthenium on SiO₂ without
18 any treatment showing macrosize defects.

19
20 Fig. 1B illustrates deposited ruthenium with oxygen
21 plasma treatment showing defect free thin film
22 deposition.

23
24 Fig. 2. illustrates x-ray diffraction data of ruthenium
25 thermal ALD films with a PE-ALD ruthenium layer.

26
27 Fig. 3. is an atomic force microscope image of a
28 ruthenium thermal ALD layer with PE-ALD Ru layer on
29 SiO₂.

1 DESCRIPTION OF THE INVENTION

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3 Variations described for the present invention can
4 be realized in any combination desirable for each
5 particular application. Thus particular limitations,
6 and/or embodiment enhancements described herein, which
7 may have particular advantages to the particular
8 application need not be used for all applications.
9 Also, it should be realized that not all limitations
10 need be implemented in methods, systems and/or
11 apparatus including one or more concepts of the present
12 invention.

13

14 An apparatus which may be used to perform the method in
15 accordance with the invention is described in the above
16 mentioned paper entitled Plasma-Enhanced Atomic Layer
17 Deposition of Ta and Ti For Interconnect Diffusion
18 Barriers by S.M. Rossnagel, J. Vac. Sci. Technol.
19 B18(4), July/Aug. 2000. The teachings of this paper
20 are incorporated herein by reference in their entirety.

21

22 Such noncommercial or a commercial atomic layer
23 deposition (ALD) chamber can be used. Sample sizes as
24 large as 200 mm diameter can be loaded and the chamber
25 can be pumped by a reactive-gas grade turbo molecular
26 pump with a working base pressure of 10^{-7} Torr. The
27 sample heating can be done using a ceramic resistive
28 heating plate, providing growth temperatures up to 450
29 °C, with the processes typically running at 350 °C. The
30 temperature can be controlled by varying current to the

1 heater, which can be previously calibrated against a
2 thermocouple attached to the sample. Solid $\text{Ru}(\text{Cp})_2$
3 (powder) contained in a glass tube can be used as the
4 metal precursor. Other metal organic Ru precursors
5 including $\text{Ru}(\text{EtCp})_2$ (bis (ethylcyclopentadienyl))
6 ruthenium) or $\text{Ru}(\text{OD})_3$ ((2,4-dimethylpentadienyl)
7 (ethylcyclopentadienyl)ruthenium) (also known as DER)
8 can be used for the same purpose. The glass tube is
9 maintained at 80 °C to develop adequate vapor pressure
10 and all the delivery lines are heated to between
11 90-110°C to prohibit condensation of the precursor. To
12 improve the delivery, argon is used as a carrier gas
13 and the flow is controlled by a mass flow controller
14 upstream from the source tube.

15

16 The RF plasma source, which includes a quartz tube
17 wrapped with a copper coil, can be used to produce
18 plasma. Oxygen, nitrogen, and hydrogen flows are
19 controlled by a leak valve or mass flow controller
20 (MFC).

21

22 The deposition cycle includes the following steps:
23 exposing the substrate to greater than 1,000 Langmuirs
24 (a measure of the net flux of gas atoms that impact a
25 unit area) of $\text{Ru}(\text{Cp})_2$ carried by argon gas, evacuating
26 the chamber, opening the gate valve for the RF source
27 and the gas valve for hydrogen for PE-ALD of ruthenium
28 or the oxygen valve for thermal ALD of ruthenium, and
29 shutting off the valves for evacuation. No purging gas
30 is used between $\text{Ru}(\text{Cp})_2$ and oxygen (or atomic H)

1 exposure, but using a purging gas does not change the
2 result. The films are deposited on 5000 Å SiO₂
3 thermally grown on Si substrates. However, the
4 invention is not limited to a SiO₂ substrate, but
5 includes various other dielectric materials including
6 SiCO, MSQ (methyl silsesquioxane), and HSQ (hydrogen
7 silsesquioxane) and other low k materials, and high k
8 oxide substrates (those having a dielectric constant of
9 greater than 4.0, which is the dielectric constant of
10 SiO₂). The film composition and thickness can be
11 determined by Rutherford backscattering spectrometry
12 (RBS). The microstructures are analyzed using X-ray
13 diffraction (XRD) and morphology and roughness by
14 atomic force microscopy (AFM).

15
16 The typical growth procedure includes 4 seconds of
17 Ru(Cp)₂ exposure at 4 sccm of flow rate, 2 seconds of
18 pump out, 2 seconds of O₂ flow at 30 sccm, and 2
19 seconds of pumping out. However, these conditions are
20 provided only by way of example and the invention is
21 not be limited to these specific process time. The
22 growth temperature is typically 350 °C, but growth
23 temperatures of 200 - 400 °C are also useful. Further,
24 ALD ruthenium can be deposited at different flow rate
25 of precursors. At oxygen flow rate higher than 40 sccm,
26 the deposited ruthenium film has a quite rough, milky
27 surface. However, at low flow rate, a mirror like
28 smooth surface is obtained.

29

1 The thermal ALD of ruthenium on SiO₂ shows that
2 deposition did not occur everywhere on the substrates
3 and macrosize defects may be seen as in Fig. 1a. This
4 is evidence of the poor nucleation of ALD ruthenium on
5 SiO₂ surfaces. RBS has shown that the carbon content is
6 below the detection limit of RBS (typically below 2%),
7 and oxygen content is very low; typically below 3%. The
8 deposition rate is 1-1.1 Å/cycle and the resistivity is
9 14-16 μΩcm.

10

11 Example

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13 To deposit nucleation problem free ALD ruthenium on
14 SiO₂, the substrates are exposed to the plasma prior to
15 the ALD of ruthenium for 10 minutes at the deposition
16 temperature. Nitrogen, oxygen and hydrogen plasma may
17 be used at 500 Watts of plasma power. In general,
18 hydrogen plasma exposure does not, in and of itself,
19 produce any significant improvement in terms of
20 producing a uniform layer. However, oxygen plasma
21 exposed SiO₂ produces very uniform, clean looking
22 deposition on the substrates. Eight inch (20.3 cm) SiO₂
23 wafers are used for measurements of uniformity. In
24 terms of sheet resistance, the uniformity of the
25 deposited ruthenium films exhibits less than 5%
26 variation in sheet resistance, without any bare surface
27 spots. Similar improvement is also obtained by nitrogen
28 exposure for 10 minutes on SiO₂ substrates. The clean,
29 macroscopic defect free ruthenium metal films deposited
30 by ALD is shown in Fig. 1b.

Comparison Example

PE-ALD using $\text{Ru}(\text{Cp})_2$ and hydrogen plasma is attempted under the same deposition conditions, as above. The deposited ruthenium layer thickness is very small, and the sheet resistance is immeasurable (typically having a value greater than $1 \Omega\text{cm}$) even for 500 process cycles, thus indicating that any atomic hydrogen which may be present does not effectively react with $\text{Ru}(\text{Cp})_2$ adsorbed on the SiO_2 from the previous cycles. On the other hand, it appears that molecular oxygen oxidatively dissociates the ligands of metal precursors, producing a thin film by ALD. However, the subsequent thermal ALD of ruthenium on a 100 cycle deposition of this very thin ruthenium PE-ALD film on SiO_2 shows uniform ruthenium deposition, which is confirmed by electrical, sheet resistance measurements. Thus, the PE-ALD ruthenium provides a very thin ruthenium layer for enabling uniform deposition of ruthenium film by thermal ALD on this very thin layer.

Fig. 2 shows the x-ray diffraction spectra of thin ruthenium films deposited by thermal ALD for 300 cycles on the 100 cycle deposit of ruthenium by the PE-ALD process. The x-ray diffraction spectra shows that the deposited film is hexagonal ruthenium metal film without any peaks related to ruthenium oxide (RuO_2).

Fig. 3 shows the results of atomic force microscope measurements of the thermal ALD ruthenium film

1 deposited on the PE-ALD ruthenium layer. There is no
2 evidence of defects, indicating that the entire surface
3 is covered by ruthenium metal film evenly, as aided by
4 the presence of the PE-ALD ruthenium underlayer.

5

6 Using this method, nucleation layer free ruthenium
7 films are deposited on dielectric surfaces, thus having
8 application as a direct plating layer for copper
9 interconnects. The PVD seed layer deposition of
10 ruthenium prior to ruthenium ALD cannot be implemented
11 for semiconductor devices with nanoscale via size, due
12 to the limited conformality of the PVD process.
13 However, by using the present invention, a thin
14 conformal layer of ruthenium is deposited inside of the
15 vias and trenches formed on various dielectrics. Copper
16 electrodeposition can be performed evenly on these
17 ruthenium layers.

18

19 Direct deposition of ruthenium by ALD also is essential
20 for the fabrication of dual work function metal gate
21 CMOS devices. Ruthenium is one of the few metals having
22 the proper work function for p-FET devices and the
23 deposition of ruthenium directly on gate oxide is very
24 important. In this case the use of a ruthenium PVD seed
25 layer is hardly useful due to possible damage by the
26 PVD process. The use of other materials as a nucleation
27 aiding layer cannot be considered for this purpose.

28

29 It is noted that the foregoing has outlined some of the
30 more pertinent objects and embodiments of the present
31 invention. The concepts of this invention may be used

1 for many applications. Thus, although the description
2 is made for particular arrangements and methods, the
3 intent and concept of the invention is suitable and
4 applicable to other arrangements and applications. It
5 will be clear to those skilled in the art that other
6 modifications to the disclosed embodiments can be
7 effected without departing from the spirit and scope of
8 the invention. The described embodiments ought to be
9 construed to be merely illustrative of some of the more
10 prominent features and applications of the invention.
11 Other beneficial results can be realized by applying
12 the disclosed invention in a different manner or
13 modifying the invention in ways known to those familiar
14 with the art. Thus, it should be understood that the
15 embodiments has been provided as an example and not as
16 a limitation. The scope of the invention is defined by
17 the appended claims.